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EFFECT OF SOIL IRRIGATION WITH WASTEWATER ON NI FRACTIONS IN SOME CONTAMINATED SOILS IN EGYPT.

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Abstract:-

In this study Ni species were determined using a sequential extraction technique. The method consists of sequential extraction of the soil with different solutions, and it is designed to separate into six operationally defined fractions namely water soluble, exchangeable, carbonate bound, Fe-Mn oxides bound, organic bound and residual fractions. The objectives of this study were to investigate nickel forms in tested soils and to determine the effect of industrial wastewater effluent irrigation on the metal fractions in soil. Data showed a remarkable increase in all tested Ni-forms in polluted soil. It could be concluded that soil composition has been changed with depth. Especially under such condition whereas, metal soluble organic compounds found in wastewater may precipitate and percolates through soil and may transport soluble Ni with the soil solution.

Keywords: *Soil contamination, wastewater irrigation, Nickel fraction*

INTRODUCTION

The content of both total and available Ni in soil is affected by different activities affecting the soil environment. Metal contaminants in soil environments derived from applications of industrial wastewater have clearly established the need for research on bioavailability and potential health risks. Alloway, (1995) reported that Ni recently has become a serious pollutant that is released in the emissions from metal processing operations and from the increasing combustion of coal and oil. Also application of sludge and certain phosphate fertilizers may be important sources of Ni in soils.

Determining the total content of heavy metals and their chemical fraction may provide useful information about metal bioavailability and toxicity to the plant, so fraction analysis is usually employed to characterize the behavior of heavy metals in soil [Lukowski and Wiater (2009); Han et al., (2007); and Walter and Cuevas (1999)]. Various chemical extraction methods have been developed to indirectly assess the association of metals with various soil components (Madden, 1988; Tessier et al., 1979). Tessier et al., (1979) were among the first to develop the procedure of sequential extraction to determine the speciation of particular trace metal in soils. Several other Kinetic fractionation methods have been developed.

All procedures are based on the assumption that the following species of metals exist in soils: 1) water soluble (e.g., in soil solution), 2) Exchangeable, 3) Organically bound, 4) Occluded in Fe and Mn oxides, 5) Definite compounds (e.g. metal carbonates, phosphates, sulfides), 6) Structurally bound in silicates (residual fraction). The soluble plus exchangeable fraction characterized the mobile species of some metals in soils. The other metal fractions are more or less immobile. The mobilization of metals from these fractions, or transformation of mobile to immobile metal species is often a slow process which is strongly controlled by reaction kinetics (Brummer et al., 1988). The observed variability in soil trace elements response to various chemical extractants suggests that, at least for some purposes, sequential extractions of soils may yield more information than single extractions (Jones, 1987).

Sequential chemical fractionation techniques separate trace elements into different operationally defined soil fractions by subjecting the soil to a series of chemical reagents, each more destructive or using a different chemical reaction than the previous one (Zufiaurre et al. 1998; Tessier, et al., 1979; Morabito 1995). The Tessier scheme is still the most effective method to devise fractions from total metals [Silveria et al., (2006) and Tessier, et al., (1979)]. Such information will enhance both human health and decisions about remediation efforts (Chaney et. al., 2003).

Kabata-Pendias and Pendias (1992) mentioned that the behavior and especially the phyto-availability of cations in soils are governed predominately by their speciation as well as by several soil properties. The speciation and localization of metallic contaminants in soils are related to their chemistry inherited from parent materials as well as at the time of impaction.

The objectives of this study were to investigate Ni forms in tested soils and to determine the effect of irrigation with industrial wastewater effluent on the metal fractions in soil.

Materials and Methods

Soil sampling

Fifteen soil samples were chosen from different locations (five different locations at north greater Cairo, Egypt) to represent different soils (alluvial and sandy) as well as different sources of contaminated wastewater (sewage and industrial effluent) as follows:

- Soil A: Non-polluted sandy soil from El-Gabal El-Asfer farm. (noncultivated).
- Soil B: Polluted sandy soil from El-Gabal El-Asfar farm. (subjected to sewage effluent irrigation for more than 75 years).
- Soil C: Non-polluted clayey soil from Bahteem area (irrigated with regular Nile water).
- Soil D: Polluted clayey soil clayey from Bahteem area (subjected **to** sewage effluent irrigation for more than 30 years).
- Soil E: Polluted clayey soil from Mostorud area (irrigated with contaminated water for more than 30 years due to direct discharge of industrial wastewater to irrigation water canals). The non-polluted soil of this group is soil C.

Soil samples were collected at three depths (i.e. 0-20 cm, 20-40 cm and 40-60 cm). The samples were air dried, crushed to pass a 2.0 mm sieve then the soil analysis were conducted according to the standard soil methods by Page et al., (1982).

Nickel fractionation:

The method for trace elements fractionation proposed by Tessier et al., (1979) was followed for the determination of Ni forms in soil sample. The method consists of sequential extraction of the soil with different solutions, and it is designed to separate heavy metals into six operationally defined fractions. The classifications are: exchangeable fraction (EXC-F), carbonate bound fraction (CAB-F), Fe-Mn oxidebound fraction (FMO-F), organic-bound fraction (OM-F), and residual fraction (RES-F) [Tessier, et al., 1979]. A summary of the procedure is as follow:

Table (1) Some Physical and Chemical Properties of the Experimental Soils.

Samples Location	Particle Size Distribution (%)				Soil texture	pH	E.C. mmhos/cm.	$CaCO_3$ (%)	O.M (%)	CEC meq/100g soil
	Coarse sand (2-0.2 mm)	Fine Sand (0.2-0.02 mm)	Silt (0.02-0.002 mm)	Clay (<0.002 mm)						
El-Gabal El-Asfar (control) Soil A	64.94	25.57	0.80	8.69	Sandy	7.27	2.29	1.85	0.38	2.81
El-Gabal El-Asfar Soil B	58.02	21.81	0.84	19.33	Sandy loam	6.91	1.23	0.70	6.17	13.26
Bahtem (control) Soil C	5.45	23.23	22.41	48.91	Clayey	7.50	4.49	2.37	1.73	27.20
Bahtem Soil D	5.67	21.53	20.80	52.00	Clayey	7.73	4.05	2.19	4.80	32.16
Mostorud Soil E	17.62	13.87	24.31	44.20	Clayey	6.74	8.43	1.60	7.99	37.44

One gram of each dry soil is weighed into a 40-ml polycarbonate centrifuge tube and the following fractions obtained:

- Water-soluble: soil sample extracted with 15 ml of deionized water for 2 hours.
- Exchangeable: The residue from water-soluble fraction is extracted with 8 ml of 1 *M* $MgCl_2$ (pH = 7.0) for 1 hour with continuous agitation.
- Carbonate bound: The residue from exchangeable fraction is extracted with 8 ml *M* sodium acetate (NaOAc), adjusted to pH = 5.0 HOAc, for 5 hours with continuous agitation.
- Fe-Mn oxides-bound: The residue from carbonate fraction is extracted with 20ml of 0.04 *M* hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25% (v/v) acetic acid (HOAc) at 96°C with occasional agitation for 6 hours.
- Organic-bound: The residue from Fe-Mn oxides fraction is extracted with 3 ml of 0.02 *M* HNO_3 and 5 ml of 30% H_2O_2 (adjusted to pH = 2.0 with HNO_3). The mixture is heated to 85°C for 2 hours, with occasional agitation. A second 3 ml aliquot of 30% H_2O_2 (adjusted to pH = 2.0 with HNO_3), is added and the mixture heated again to 85°C for 3 hours with intermittent agitation. After cooling, 5 ml of 3.2 *M* NH_4OAc in 20% (v/v) HNO_3 is added and the samples diluted to 20 ml and agitated continuously for 30 minutes.
- Residual: The residual from organic fraction was placed in platinum crucible and digested with hydrofluoric acid according to Jackson (1973).

Following each extraction, mixture was centrifuged at 5000 rpm for 10 minutes. Prior to the start of the next extraction step, the residues were shaken with 8-ml water for 30 minutes, centrifuged, and wash solutions discarded. All soil extractants were analyzed for Ni, using AAS technique.

Results and Discussions

Total Ni in soils:

Result of soil total-Ni indicated the serious accumulation of Ni in soils subjected to prolonged irrigation with wastewater as shown in Table (2). As shown, total-Ni in the tested soils exceeds the permissible levels (250 ppm Ni according to Kabata-Pendias and Pendias (1992) by several orders of magnitude particularly at the surface and subsurface layers. The highest accumulation of total Ni down to depth 60 cm was observed in the case of soil E. This high accumulation is a result of irrigating these soils with industrial wastewater drain, which contains suspended particulate with high levels of Ni (as high as 2229 mg Ni / L) as reported by Abdel –Sabour *et al.,* (1998). In Egypt, total content of Ni in the alluvial soils of the Nile valley and Delta ranges between 21.0 and 44.0 ppm (average = 32.0 ppm) as reported by Rashad et al (1995). However, very small amount of this total was found in available form, it ranged between 0.38 and 1.04 ppm (with an average=0.66 ppm). Other soils of Egypt have different content of both total and available forms.

Total Ni determined by summation of extracted Ni fractions in soil (*i.e.* soluble + exchangeable + carbonate + occluded in Fe & Mn oxide + organic fraction + residual fraction) represent the calculated total Ni in soil. Comparing the calculated values with the total Ni values determined by Atomic Absorption Spectroscopy (AAS) technique showed a non-significant differences (computed T-test = 1.92 and p-value =0.076). Fig. (1) Shows a significant correlation between total Ni as calculated by the summation of sequential extraction procedure and total Ni as determined by AAS (R^2= 0.97).

Many studies were carried out on the effect of using industrial wastewater or sewage water for irrigation. Data of El-Gamal (1980) indicate that total content in El-Gabal ElAsfar soils irrigated with sewage water for several years ranges from 162 to 1611 ppm with an average of 675 ppm, while the DTPA extractable Ni varies from 0 to 4.6 ppm with an average of 2.1 ppm. El-Leith (1986) studied the effect of industrial activities and highways on soil pollution with Ni on Nile Delta. He found that Ni content in the industrial areas varies largely due to the nature and composition of industrial wastes. He also found that total Ni content in the surface layer of soil irrigated with waste drain containing 27-112 ppm, and extractable Ni from 0.02 to 1.76 ppm. Similar results were recorded by El-Saady (1994) and Rashad (1986). Hassan (1997) studied the effect of using different industrial wastewater for irrigating some soils in Shoubra El-Khiema. He found that total Ni in the surface layers of the uncultivated soils was 43.5 ppm, while it ranges between 51.0 and 177.0 in the soils irrigated with different industrial wastes. The DTPA extractable Ni followed the same trend.

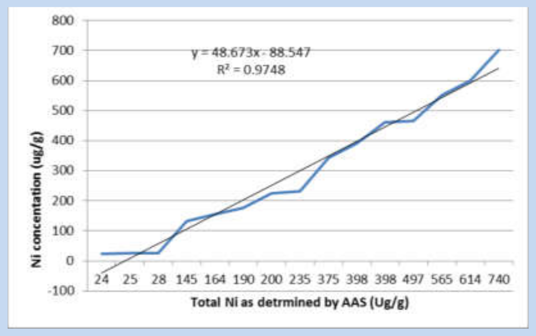


Fig. (1) Correlation between total Ni as calculated by the summation of sequential extraction procedure and total Ni as determined by AAS (µg/g)

Nickel fractions:
Nickel fractions of the soils (Table 3) showed that the major amounts of Ni in the tested soils were associated with the structurally bound in silicates (residual fraction). The residual fraction represented from 43.47 to 70.96 % of the total Ni in the tested soils (Table 4). The highest residual- Ni content was always found at the surface soil layer (0-20 cm) except for soil D. Ma and Rao (1997) added that the greater percentage of Ni in the residual fraction probably reflects the greater tendency of Ni to become unavailable. Similar results were found by El-Gendi *et al.,* (1997) who found that Ni residual fraction is the prevailing form, followed by organic fraction; oxides bound then Ni-carbonates fraction and finally the exchangeable form in sandy soils of Egypt.

Nickel occluded in iron and manganese oxides fraction constituted from 5.61 up to 34.84% of total Ni in the tested soils. The lowest values of Ni- occluded in Fe and Mn oxide fraction in case of soil E may be explained by the accumulation of soluble organic compounds throughout the soil profile due to the prolonged irrigation with industrial wastewater enriched by organic waste. This finding is confirmed by the remarkable increase in Ni-organically bound fraction in soil E compared with its relevant soil C and D (Table 3); Hence, the percentage of the accumulation of soil organic matter throughout the soil profile was 6.1 up to 7.99 % as shown in Table (1).

Thus, the data show obviously that soil contaminated due to irrigation with either sewage effluent or industrial wastewater has resulted in a significant increase in both Ni-organic and Ni occluded in Fe and Mn oxide fractions followed by the carbonate fraction. Everhart et al., (2006) indicated that most of the Ni and Fe in two contaminated soils were complexed with Fe and Mn oxides. This was expected due to the high oxide content in both soils. The Quarry Muck soils contained a larger Ni and Fe fraction associated with organic matter, as indicated by the HNO3 and 30% H2O2 extractions, compared to the Welland Loam soils. This was expected since the Muck soils contained approximately, on average, 60% more organic matter than the Loam soils.

Nickel in sewage sludge is present mainly in organic chelated forms, which is readily available to plants and therefore may be highly phyto-toxic. Soil treatments, such as addition of lime, phosphate or organic matter, are known to decrease Ni availability to plants. Heavy metal species entering soils due to sewage sludge application differ upon the source and the treatment of wastes. The forms associated with sesqui-oxides and with compounds bound to organic residual fractions predominate usually in sludge of municipal origin. When wastes are mixed with some industrial effluents, however, the speciation of metals greatly differs upon the discharged forms factories.

Table 3 Forms of Ni (mg /kg) in the experimental soils.

Soil	Depth cm	WS	EX	CAR	OX	ORG	RES	*TOTAL (SUM)*
Sandy and Sandy loam soil								
	0 - 20	0.10	1.69	2.08	8.45	1.90	14.00	28.22
A	20 - 40	0.08	1.50	1.82	6.90	1.60	13.40	25.30
	40 - 60	0.08	0.72	1.55	6.96	1.47	13.33	24.11
	0 - 20	1.20	31.33	16.38	124.20	62.10	330.20	565.41
B	20 - 40	0.68	26.46	11.96	108.70	47.40	202.50	397.70
	40 - 60	0.30	12.32	6.76	68.90	24.60	86.80	199.68
Clayey soil								
	0 - 20	0.23	1.30	10.40	33.60	11.40	133.15	190.08
C	20 - 40	0.15	1.04	6.85	32.40	9.40	113.86	163.70
	40 - 60	0.15	0.89	5.20	31.20	4.80	103.20	145.44
	0 - 20	0.60	2.99	27.95	119.20	50.40	196.65	397.79
D	20 - 40	0.53	2.34	22.47	100.00	41.60	207.60	374.54
	40 - 60	0.23	2.04	15.60	82.00	10.00	125.50	235.37
	0 - 20	1.65	15.00	71.50	41.5.0	184	426.00	739.65
E	20 - 40	1.13	11.10	42.90	37.90	172.5	348.00	613.53
	40 - 60	0.60	9.90	26.00	33.20	103.5	324.00	497.20

WS: *Water-soluble fraction****.*** ***ORG:*** *Organic-bound fraction****.*** ***EX:*** *Exchangeable fraction.* ***RES:*** *Residual fraction.* ***CAR:*** *Carbonate- bound fraction.* ***SUM:*** *Summation of fractions****.*** ***OX:*** *Fe-Mn Oxides- bound fraction.*

Bloomfield (1981) stated that although organic matter is able to mobilize Ni from carbonates and oxides as well as to decrease Ni sorption on clays, the bonding of this metal to the organic ligands could not be particularly strong. Complexing ligands such as SO2^{-4} and organic acids reduce the sorption of Ni. Also, the Ni status in soils is highly dependent on the Ni content of parent rock. However, the concentration of Ni in soils also reflects soil forming processes and pollution. Canet et al. (1997) found that most of Ni was present in carbonate and residual fractions. As shown in Table 4 Ni was present in the residue fraction between 43% to 70 % of total Ni in soil.

The soluble plus exchangeable fractions characterize the mobile fraction of Ni in soils. This fraction ranged from 3.32 up to 6.82 % of total Ni in sandy soils (soil A and B). However, a lower value (0.72 to 2.25) could be observed in case of the tested clayey soils. As shown in Fig (2) the absolute values increased remarkably particularly in case of soils B and E. It is worth to mention, that a significant increase in this fraction was noticed in the contaminated soil especially in surface soil layer due to the pollution effect on the organic matter and soil pH.

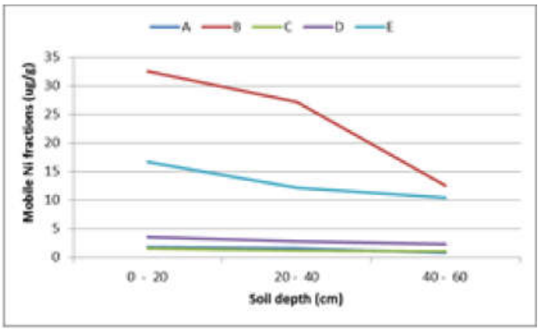
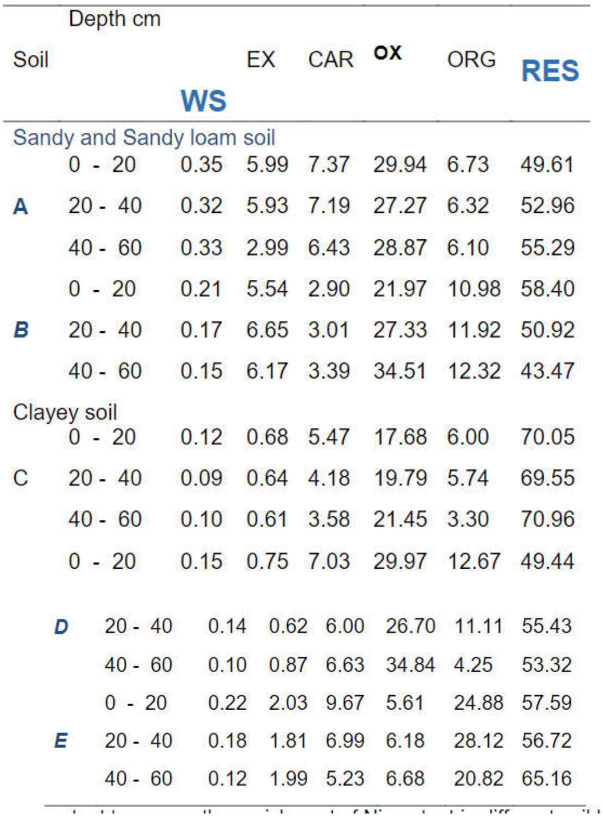


Fig. (2) Mobile Ni fraction (soluble plus exchangeable fractions) in different tested soil depths (cm) as affected by soil contamination.

Kuo and Baker (1980) reported that the solubility and exchangeability of Ni in soil increased with the decrease in soil pH. The mobilization of metals or transformation of mobile to immobile metal species is often a slow process which is strongly controlled by reaction kinetics *(Bisessar, (1989),* Brummer *et al.,* 1988).

Table 4 : Percentage of Ni forms from the total Ni in different soil layers profiles.



Soil	Depth cm	WS	EX	CAR	OX	ORG	RES
Sandy and Sandy loam soil							
A	0 - 20	0.35	5.99	7.37	29.94	6.73	49.61
	20 - 40	0.32	5.93	7.19	27.27	6.32	52.96
	40 - 60	0.33	2.99	6.43	28.87	6.10	55.29
B	0 - 20	0.21	5.54	2.90	21.97	10.98	58.40
	20 - 40	0.17	6.65	3.01	27.33	11.92	50.92
	40 - 60	0.15	6.17	3.39	34.51	12.32	43.47
Clayey soil							
C	0 - 20	0.12	0.68	5.47	17.68	6.00	70.05
	20 - 40	0.09	0.64	4.18	19.79	5.74	69.55
	40 - 60	0.10	0.61	3.58	21.45	3.30	70.96
D	0 - 20	0.15	0.75	7.03	29.97	12.67	49.44
	20 - 40	0.14	0.62	6.00	26.70	11.11	55.43
	40 - 60	0.10	0.87	6.63	34.84	4.25	53.32
E	0 - 20	0.22	2.03	9.67	5.61	24.88	57.59
	20 - 40	0.18	1.81	6.99	6.18	28.12	56.72
	40 - 60	0.12	1.99	5.23	6.68	20.82	65.16

It is very important to assess the enrichment of Ni content in different soil layers due to the pollution effect of wastewater irrigation in the tested soils compared to relevant control soil. As shown in Table (5), a drastic increase was noticed in total Ni in different soil layers, particularly in case of sandy soil (*e.g.* total Ni increased by 20, 15.7 and 8.3 folds compared to its control soil, in case of 0 -20 cm, 20-40 cm and 40-60 cm soil layer, respectively); in case of clayey soil the increase of total Ni ranged between 1.62 to 3.89 folds of its original soil (C).

The contribution percentage (enrichment ratio) of each tested Ni fraction (relative to control soil for each layer) was also calculated as shown in Table (5). Data show the remarkable increase in all tested Ni-forms in polluted soil profile. It could be concluded that soil composition has been changed with depth (from surface to subsurface layers). Especially under such conditions whereas metal soluble organic compounds found in wastewater may precipitate and percolate through soil and may transport soluble heavy metals with the soil solution.

Several workers have investigated the relationships between Ni fractions and different soil properties such as pH, organic matter content, clay content, cation exchange capacity and calcium carbonate content (Soon and Bates, 1982 and Chlopecka *et al.,* 1996). The results of statistical simple correlation among different Ni fractions and some soil properties (Table 6) showed that soil pH and CaCO3 % had a significant negative effect on total-Ni and most tested fractions. However a significant positive relations were observed with soil O.M.% and soil CEC. The relation between Ni fraction and soil clay content was not consistence in the tested clayey soil due to the non-significant variation in soil clay content. In case of sandy soil, positive relations with clay % were observed due to the relative increase in soil clay content as a result of sewage effluent irrigation. Shuman (1985) found a high correlation between CEC, organic matter, clay content with Ni removed from the various fractions.

The highly significant relations clearly indicate the importance of soil organic matter content (Nachtegaal and Sparks 2003), as shown that the main source of pollution in the tested soils is due to the suspended and soluble organic particulates found in the used wastewater for irrigation as reported by Abdel- Sabour *et al.,* (1998).

Conclusion

The soil fractions are, ideally, indicative of the potential Ni bioavailability or mobility with bioavailability and mobility decreasing in the order of the sequential extraction steps. Sequential soil extractions are useful analyses because they give a rough estimate of metal associations in soils. However, these experiments are operationally defined depending on the extractants used and do not directly identify specific metal complexes/species that are present.

Table (5): Enrichment ratio* of Ni fractions due to irrigation with wastewater in the contaminated tested soils (relative to control).

Soil	Depth cm	WS	EX	CAR	OX	ORG	RES	*TOTAL (SUM)*
Sandy soil								
B	0 - 20	12.00	18.54	7.88	14.7	32.68	23.59	20.04
	20 - 40	8.50	17.64	6.57	15.75	29.63	15.11	15.72
	40 - 60	3.75	17.11	4.36	9.90	16.73	6.51	8.28
Clayey soil								
D	0 - 20	2.61	2.30	2.69	3.55	4.42	1.48	2.09
	20 - 40	3.53	2.25	3.28	3.09	4.43	1.82	2.29
	40 - 60	1.53	2.29	3.00	2.63	2.08	1.22	1.62
E	0 - 20	7.17	11.54	6.88	1.24	16.14	3.2	3.89
	20 - 40	7.53	10.67	6.26	1.17	18.35	3.06	3.75
	40 - 60	4.00	11.12	5.00	1.06	21.56	3.14	3.42

* Enrichment ratio = $\frac{\text{Metal content of contaminated soil}}{\text{Metal content of control soil}}$

Table (6): Simple correlation coefficients between different soil properties and tested Ni fractions.

Ni-fractions	Clay(%)	pH	CEC	O.M	*CaCO3*
Sandy and Sandy loam soil					
Soluble	0.972	-0.786	0.954	0.978	-0.955
Exchangeable	0.945	-0.793	0.989	0.994	-0.977
Carbonate	0.953	-0.788	0.991	0.993	-0.981
Oxide	0.891	-0.739	0.994	0.970	-0.967
Organic	0.941	-0.773	0.994	0.992	-0.977
Residual	0.972	-0.784	0.969	0.988	-0.964
Total Ni (sum)	0.956	-0.780	0.988	0.994	-0.976
Clayey soil					
Soluble	-0.345	-0.841	0.888	0.921	-0.857
Exchangeable	-0.596	-0.948	0.768	0.946	-0.935
Carbonate	-0.324	-0.814	0.934	0.912	-0.847
Oxide	0.653	-0.397	0.311	-0.023	-0.111
Organic	-0.492	-0.921	0.769	0.958	-0.927
Residual	-0.463	-0.928	0.808	0.970	-0.953
Total (sum)	-0.368	-0.873	0.877	0.979	-0.938

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